

Effect of microhydration on the resonances of pyridine and thymine

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Synopsis We have investigated the effect of microhydration on the resonances of pyrimidine and thymine. We have performed calculations on electron scattering from pyridine-(H₂O)_n and thymine-(H₂O)_n (n=1,2,3,5) and compared the positions of the electronic resonances with those of the isolated molecules. Some interesting conclusions about microhydration effects have been obtained.

Electron scattering from polyatomic and, in particular, biological molecules has been a focus of investigations for at least a couple of decades [1]. One of the most significant applications is in the study of biological radiation damage, where the most interesting electron-induced process is dissociative electron attachment. This process is initiated by the formation of a resonance or transient negative ion. Work until recently has mainly concentrated on gas phase/isolated molecules providing insight into the collision process. However, biological radiation damage occurs in a condensed environment where all molecules with a biological function are surrounded mainly by water.

Hydrated clusters have been proposed as systems that bridge the gap between the pure gas phase and the actual environment in which these collisions take place. Small clusters can be treated using the same *ab initio* methodology as isolated molecules. Prior work using the Schwinger Multichannel method (see, for example [2]) has looked at how the hydrogen bonding of 1 or 2 water molecules to organic molecules affects the characteristics of their resonances. Freitas *et al.* established that when water acts as a hydrogen donor, resonances in the molecules are stabilized (their energy is lower) whereas when water acts as the hydrogen acceptor, they are destabilized.

We have used the R-matrix method [3] as implemented in the UKRmol+ suite to study electron scattering from pyridine-(H₂O)_n and thymine-(H₂O)_n with n=1,2,3,5. Calculations have been performed mainly at the Static-Exchange level, with the exception of pyridine-H₂O, where use of the close-coupling approximation has enabled us to look at core-excited resonances. The clusters for n>2 are

very different for these two ring molecules: in the case of pyridine, additional H₂O bond to the first H₂O, whereas for thymine additional waters attach to thymine itself. We discuss the different effect microhydration has in these two cases.

Our calculations confirm the findings of Freitas *et al.*, both in terms of the link between the stabilization/destabilization of resonances and the donor/acceptor role of H₂O in the hydrogen bonding and the approximate additivity of the effect as the number of water molecules in the cluster increases. In addition, we also show that: (i) microhydration effects can be understood in terms of an indirect (change to the molecule's geometry) and direct (actual effect of the hydrogen-bonding) contribution; (ii) the effect of each H₂O molecule depends on the binding site; (iii) this effect is different for different resonances in the system, in contradiction with prior assumptions [4].

We will discuss the possible effect of the shifts on the dissociative electron attachment processes and the link of our results to recent experiments on microsolvated uracil and thymine [5].

References

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